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(54) CROSS-LINKING OF POLYMERS

(71) We, DOW CORNING LIMITED, a British Company of 12 Whitehall, London, S.W.1. formerly Midland Silicones Limited of Reading Bridge House, Reading, Berkshire, England, do hereby declare the invention for which we pray that a Patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to improvements in or relating to the crosslinking of organic polymers.

It is known that organic polymers may be rendered crosslinkable by incorporating therein silyl groups having attached thereto hydrolysable atoms or radicals. Such silyl groups may be incorporated into the organic polymer by copolymerisation of the appropriate organic monomer with an organosilicon compound, for example, as described in our co-pending Application No. 58833/69 (Serial No. 1,329,248). The silyl groups may also be incorporated by grafting an organosilicon compound to the pre-formed organic polymer as described and claimed in U.K. Patent Specifications Nos. 1,234,034 and 1,286,460.

Crosslinking of the silyl-modified polymers prepared as described hereinabove is achieved by exposing the polymer to water in the presence of a siloxane condensation catalyst. According to the known techniques, the catalyst may be added to the bulk of the polymer prior to shaping or may be generated *in situ* as the result of the hydrolysis of acid- or base-forming groups attached to silicon atoms. In many cases, exposure of the catalysed, crosslinkable product to atmospheric moisture is sufficient to initiate the crosslinking reaction. The avoidance of premature crosslinking, particularly during storage or shaping of the polymer, therefore, sometimes presents problems. In addition, the recovery and recycling of, for example, waste extrudate is prevented if crosslinking has proceeded to any significant degree.

Some of the above recited difficulties can be overcome by formulating the crosslinkable product as a two-package system in which the catalyst is added in admixture with organic polymer which has not been modified with silyl groups. This solution is not, however, fully satisfactory as it results in dilution of the cross-linkable polymer with polymer which is not similarly cross-linkable.

We have now found that an improved method of promoting crosslinking in a silyl-modified organic polymer of the kind described above resides in contacting the polymer, usually after shaping, with an aqueous dispersion or solution of a tin carboxylate.

According to this invention, therefore, there is provided a process for effecting crosslinking in an organic polymer having chemically bonded thereto silyl groups of the general formula $-\text{SiR}_n\text{X}_{3-n}$, wherein R represents a monovalent hydrocarbon or halogenated hydrocarbon radical, X represents a hydrolysable radical and n has a value of 0, 1 or 2, comprising contacting said organic polymer with an aqueous dispersion or solution of a tin carboxylate.

The invention also includes an organic polymer whenever crosslinked by said process.

The organic polymers which may be crosslinked by the process of this invention are those having therein groups of the formula $-\text{SiR}_n\text{X}_{3-n}$, in which R is a monovalent hydrocarbon or halogenated hydrocarbon radical, for example, an alkyl radical, e.g. methyl, ethyl, propyl, octyl, decyl or tetradecyl, an aryl radical, e.g. phenyl, benzyl or tolyl or haloalkyl or haloaryl e.g. chloropropyl, 3,3,3 - trifluoropropyl or bromophenyl. The substituent X may be any hydrolysable radical, for example, an acyloxy radical, e.g. formyloxy, acetoxy or propionoxy, an oximo radical e.g. $-\text{ON}=\text{C}(\text{CH}_3)(\text{C}_2\text{H}_5)$ or $-\text{ON}=\text{C}(\text{CH}_3)(\text{C}_6\text{H}_5)$ or an alkoxy or alkoxyalkoxy radical, e.g. methoxy, ethoxy, propoxy or

methoxyethoxy. Preferably, the X substituents are alkoxy or alkoxyalkoxy radicals having less than 4 carbon atoms and n is zero.

Any silyl-modified organic polymer may be cross-linked employing the process of this invention. Examples of such organic polymers are polyethylene, ethylene-propylene copolymers, polyvinyl chloride, polystyrene, copolymers of vinyl chloride with monomers such as alkyl acrylates, polymethacrylates, polyamides, polyesters and polyacrylonitrile. The process of this invention is of particular interest with regard to the cross-linking of polyethylene and polyvinyl chloride.

Methods for preparing the silyl-modified polymers which can be cross-linked by the process of this invention are described, for example, in U.K. Patent Specifications Nos. 1,234,034, 1,286,460 and 1,329,248 the disclosures of which are incorporated herein by reference. Such methods include subjecting the organic polymer to mechanical working in the presence of an organosilicon compound having in the molecule at least one silicon-bonded hydrolysable radical and a silicon-bonded radical reactive which the free radical sites generated in the organic polymer. In a preferred method of applying this process in the modification of polyolefins, which is described in U.K. Patent Specification No. 1,286,460, the polyolefin is reacted with the organosilicon compound in the presence of a compound, e.g. an organic peroxide, capable of generating free radical sites in the polyolefin. According to the process, the reaction is carried out at a temperature above 140°C and the said free radical generating compound has a half-life at the reaction temperature of less than 6 minutes.

According to the process described in U.K. Patent Specification No. 1,329,248 a cross-linkable vinyl chloride polymer is prepared by copolymerising, under bulk copolymerisation conditions, vinyl chloride and a silane having a silicon-bonded unsaturated radical and silicon-bonded hydrolysable radicals.

The nature of the chemical linkage through which the silyl group is bonded to the organic polymer backbone will depend on the method employed to prepare the cross-linkable polymer and on the organosilicon compound. For example, when the method of preparation involves free radical-induced modification of the preformed polymer with vinyl triethoxysilane, the silyl group is believed to become attached to the polymer backbone through a $-\text{CH}_2\text{CH}_2-$ radical. When the cross-linkable polymer is prepared by the copolymerisation of, for example, vinyl chloride and vinyl triethoxysilane, the silyl group will be attached directly to a carbon atom in the polymer backbone. When present, the linking group will normally be a divalent hydrocarbon radical or a divalent radical composed of carbon, hydrogen and oxygen wherein the oxygen is

present in the form of ether linkages. However, the precise nature of the linking group is not critical to the success of this invention.

In accordance with the process of this invention, cross-linking of the cross-linkable organic polymer is effected by contact with a dispersion or solution of a tin carboxylate. Usually the polymer will be shaped, for example by an extrusion or moulding operation, prior to contact with the solution or emulsion.

The tin carboxylate may be any organic compound of tin containing a carboxylate group. Such compounds include those in which the tin is divalent, e.g. as in stannous octoate, as well as those in which it is tetravalent, e.g. as in the mono-, di- and tri- alkyltin carboxylates. The tin carboxylates are a well known class of compounds and may be readily prepared by well-known techniques, for example by reacting organotin oxides (or hydroxides) and carboxylic acids or anhydrides. Specific examples of tin carboxylates are tributyltin laurate, dibutyltin dilaurate, dibutyltin di-2-ethylhexoate, dioctyltin di-2-ethylhexoate, butyltin triacetate, butyltin trilaurate, octyltin trilaurate, dibutyltin diacetate, stannous octoate and stannous oleate. The preferred tin carboxylates for use in the process of this invention are the dialkyltin dicarboxylates and the alkyltin tricarboxylates, dibutyltin dilaurate and dibutyltin diacetate being most preferred. When the product made from the cross-linked polymer is likely to come into contact with edible materials, e.g. food or water, it is desirable that the tin carboxylate employed is either such that it will not be leached from the product in use and/or is substantially non-toxic.

As the tin carboxylates are normally insoluble, or only slightly soluble, in water, they will generally be employed in the form of an aqueous dispersion. Where a dispersion is employed, it may be prepared using conventional techniques and, when necessary, dispersing aids such as emulsifying agents. The concentration of the tin carboxylate in the solution or dispersion is not critical. It may be varied widely depending on such factors as the rate of cross-linking desired and the operating conditions. For example a concentrated solution or dispersion may be more appropriate for use in a continuous process where frequent topping up with tin carboxylate is inconvenient or otherwise undesirable. In general we prefer to employ a solution or dispersion containing from 0.01 to 20 per cent by weight of the tin carboxylate. However, solutions or dispersions containing percentages of tin carboxylate outside this range may be effectively employed.

To expedite the cross-linking reaction, the solution or emulsion of the tin carboxylate is preferably maintained at a temperature of at

least 50°C, preferably from 50 to 100°C. The duration of contact between the polymer and the solution or emulsion will depend, for example, on the particular type of polymer, its shape and dimensions, and on the degree of cross-linking desired. For example, when the shaped articles are individual items such as bottles, they may be immersed in the solution or emulsion for many hours. When the shaping process is continuous extrusion, e.g. as in the production of film, a residence time of 30 minutes or less may be more appropriate.

Cross-linked organic polymers prepared according to this invention may be employed in a variety of applications where the corresponding non-cross-linked material may be unsuitable. In particular, polyethylene and polyvinyl chloride which have been cross-linked by the process are useful for the production of hot water pipes, bottles, electrical insulating components, films and other articles.

The following examples, in which the parts are expressed by weight, illustrate the invention. The words Shell, Teepol and Mellite referred to in the examples are registered trade marks.

Example 1.

100 parts of low density polyethylene granules (Shell 25-200) having a melt index of 20g./10 min. were coated by tumbling with 2 parts of vinyl trimethoxysilane having dis-

solved in it 0.17 parts of dicumyl peroxide. Tumbling was continued until all of the liquid had been taken up by the granule surfaces.

The composition was then passed through a Buss PR46 Ko Kneader. Operating temperatures in the Ko Kneader were 178°C for the kneader and 184°C for the crosshead extruder. The product obtained was a graft copolymer of polyethylene and vinyl trimethoxysilane having a melt index of 3.4 g/10 min.

A sheet having a thickness of 0.068 inch was formed from the graft copolymer by compression moulding. Portions of the sheet were immersed in an aqueous emulsion of dibutyltin dilaurate which had been prepared from 10 ml. of dibutyltin dilaurate and 100 ml. of water using 1 ml. of Teepol (sodium salt of secondary alkyl sulphate) as emulsifying agent. The portions were immersed for periods of 1 hour and 2 hours during which the emulsion was maintained at 90°C. For comparison, portions of the sheet were also immersed for similar periods in boiling water.

The gel content of the treated portions, which indicates the degree of cross-linking which has occurred, was then determined. This was carried out by immersing weighed samples in boiling xylene for 20 hours and measuring the percentage insoluble material remaining. The results were as follows:

	Immersion in Water	Immersion in Catalyst Emulsion
1 hour	8.5% by weight	47.7% by weight
2 hours	4.1% by weight	61.5% by weight

Example 2.

Using the procedure described in Example 1 a graft copolymer was prepared using 100 parts of low density polyethylene granules (XNM 68) having a nominal melt index of 6.8 g/10 min, 2 parts of vinyl trimethoxysilane and 0.216 parts of dicumyl peroxide. The operating temperature of the Buss Ko Kneader was 220°C and throughout was 170 g/min. The resulting graft copolymer had a melt index of 1.2 g/10 min.

Sheets of the copolymer having a thickness of 0.125 inch were prepared by compression moulding. Portions of the sheets were then

immersed for periods of 1 hour and 3 hours in an aqueous emulsion containing 0.1% by weight of dibutyltin dilaurate, the emulsifying agent being Teepol. During immersion the temperature of the emulsion was maintained at 100°C. Additional portions of the sheets were also immersed in an emulsion (at 100°C) containing 0.0125% by weight of dibutyltin dilaurate.

Gel contents, that is percentage insoluble material, were measured on all samples according to the method described in Example 1. The results obtained were as follows:

	0.1% Emulsion		0.0125% Emulsion		
	1 hr.	3 hr.	1 hr.	3 hr.	22 hr.
Gel content (% by wt.)	72	83	24	68	84

Example 3.

5 A strong walled glass tube having a length of about 25 cm. and internal diameter of about 2.5 cm. was dried at 120°C for one hour and allowed to cool in an atmosphere of nitrogen. Azobisisobutyronitrile (0.05 gms.) and vinyltriethoxysilane (1g.) were then introduced into the tube and the contents cooled by immersion in a mixture of isopropanol and solid carbon dioxide. Vinyl chloride (50g.), which had been purified by passage over flake potassium hydroxide, was introduced in liquid form into the tube, the tube immersed in liquid nitrogen and then sealed.

10 The sealed glass tube was then placed in a protective steel tube and both immersed in a water bath at 50°C. After 16 hours the tube was cooled in liquid nitrogen, the seal on the glass tube was broken and the solid plug of copolymer recovered. The copolymer had a number average molecular weight in the range 60,000—80,000. The copolymer was granulated and then mixed on a rotating ball mill for 6 hours with 3% by weight of Mellite 101 (a cadmium laurate-barium laurate stabiliser) and 1% by weight of Mellite 310 (a phosphite chelating agent). The blended granules were fluffed for 10 minutes on a two roll mill at 155°C before sheeting off. Sheets of the resin were then pressed at 170°C under 2,000 p.s.i. to give translucent yellow sheets of 0.05 inch thickness.

35 Test pieces taken from the sheet were cross-linked by immersion in an aqueous emulsion of dibutyltin dilaurate which had been prepared from 5 mls. of dibutyltin dilaurate and 100 mls. of water using 0.5 ml. Teepol as the emulsifying agent. The portions of sheet were immersed for a period of 24 hours during which time the emulsion was maintained at 100°C.

45 Gel content measurements were carried out on the test pieces using boiling tetrahydrofuran as the extraction solvent. The extraction

time was 20 hours. The gel (i.e. insoluble) content of the cross-linked material was found to be 94% by weight. When the experiment was repeated using vinyltrimethoxysilane (1g.) in place of the vinyl-triethoxysilane the resulting cross-linked copolymer had a gel content of 97%.

WHAT WE CLAIM IS:—

1. A process for effecting cross-linking in an organic polymer having chemically bonded thereto silyl groups of the general formula $-\text{SiR}_n\text{X}_{3-n}$, wherein R represents a monovalent hydrocarbon or halogenated hydrocarbon radical, X represents a hydrolysable radical and n has a value of 0, 1 or 2, said process comprising contacting said organic polymer with an aqueous dispersion or solution of a tin carboxylate.

2. A process as claimed in claim 1 wherein the organic polymer is polyethylene or polyvinyl chloride.

3. A process as claimed in claim 1 or claim 2 wherein X represents an alkoxy or alkoxyalkoxy radical having less than 4 carbon atoms and n is 0.

4. A process as claimed in any one of the preceding claims wherein the tin carboxylate is dibutyltin dilaurate or dibutyltin diacetate.

5. A process as claimed in any one of the preceding claims wherein the aqueous dispersion or solution contains from 0.01 to 20 per cent by weight of the tin carboxylate.

6. A process as claimed in any one of the preceding claims wherein the aqueous solution or dispersion is maintained at a temperature of from 50 to 100°C.

7. A process for effecting cross-linking in an organic polymer substantially as described with reference to the Examples.

8. A cross-linked organic polymer whenever prepared by the process claimed in any one of the preceding claims.

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